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REDUCTION OF CARBONYL COMPOUNDS VIA HYDROSILYLATION

II *. ASYMMETRIC REDUCTION OF KETONES VIA HYDROSILYLATION CATALYZED BY A RHODIUM(I) COMPLEX WITH CHIRAL PHOSPHINE LIGANDS

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Summary

Effective asymmetric reduction of alkyl phenyl, dialkyl and alkyl cyclohexyl ketones has been achieved via hydrosilylation, catalyzed by a rhodium(I) complex with optically active phosphine ligands using various hydrosilanes. A mechanism of the induction of asymmetry is proposed in view of the stereochemical course of the reaction.

Introduction

Although the homogeneous hydrogenation of carbon—carbon multiple bonds catalyzed by various transition metal complexes has been extensively studied [1], that of carbon—oxygen double bonds has received relatively little attention. Thus, there had been only a few papers [2] before Schrock and Osborn reported [3] in 1970 that cationic rhodium complexes with relatively basic phosphines as ligands catalyze the reduction of ketones under mild conditions. This is partly due to the fact that the Wilkinson's type non-cationic rhodium(I) complexes lack activity toward the hydrogenation of carbonyl functionalities [4] and that these complexes also catalyze the decarbonylation of carbonyl compounds, especially of aldehydes [4,5]. On the basis of these findings a catalytic asymmetric hydrogenation of ketones has been achieved with low optical yields in 1972 [6]. Ohgo and coworkers also reported the asymmetric homogeneous reduction of carbonyl groups, but except for the rather special case of the reduction of benzil to benzoin in 78% e.e. with Co(dimethyl-

* See ref. 13c for Part I.

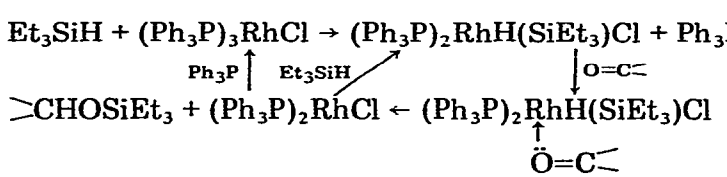
glyoxymato)$_2$(quinine)(benzylamine) as a catalyst, the product alcohols were obtained with a low enantiomeric excess [7].

A similar trend can be seen in catalytic hydrosilylation. The hydrosilylation of olefins and acetylenes has been extensively studied in the last two decades [8]. However, hydrosilylation of carbon—hetero atom multiple bonds has received less attention. Since a silicon—oxygen bond or a silicon—nitrogen bond can be easily hydrolyzed, the hydrosilylation of carbonyl compounds or imines is equivalent to hydrogenation. Thus, the catalytic hydrosilylation of the compounds containing such a double bond may provide a powerful new reduction method if the reaction is achieved effectively.

Calas [9], Frainnet [10], Petrov [11] and their coworkers studied the catalytic hydrosilylation of carbonyl compounds using zinc chloride, nickel metal and chloroplatinic acid as a catalyst. However, the required conditions for these reactions were rather drastic and the formation of side products or the isomerization of both starting materials and products were often observed. Moreover, the use of these catalysts has been restricted to hydrosilylation with monohydrosilanes. This limitation is mainly due to the fact that the disproportionation of polyhydrosilanes is also catalyzed by these substances [12]. In 1972, we found that tris(triphenylphosphine)chlororhodium was quite effective for the hydrosilylation of carbonyl compounds [13]. Corriu and Moreau also studied [14] the addition of dihydrosilanes to ketones in the presence of dichlorotris-(triphenylphosphine)ruthenium(II) as well as of the rhodium complex, but the ruthenium(II) complex appears to be less effective than the rhodium(I) complex. Thus, hydrosilylation followed by hydrolysis can serve as a powerful new method in organic synthesis and has already been developed in the selective reductions of terpene carbonyl compounds [15,16] and Schiff bases [17].

The mechanism of this reaction seems to be related to that of the hydrogenation of olefins and involves an oxidative addition of the silane to the rhodium complex leading to a complex, $(Ph_3P)_2RhH(SiR_3)Cl$. We isolated a complex of this type in which R is an ethyl group as a reaction intermediate [13]. A proposed mechanism for the reaction is depicted in Scheme 1.

SCHEME 1



Asymmetric reduction of prochiral ketones by hydrosilylation in the presence of a chiral rhodium catalyst followed by hydrolysis has been developed by four groups independently after our first report in 1972 [13] and continues to be under active investigation [18]. The first asymmetric hydrosilylation of prochiral ketones was reported by Yamamoto et al. [19] using chiral platinum complexes in 1972. This method has, however, the following disadvantages: (i) The hydrosilane which can be used for the reaction is restricted to methyldichlorosilane, i.e., trialkylsilanes cannot be employed because of their lack of reactivity. (ii) Although the optical yield is increased to some extent by employing bulky

ketones, the chemical yield of the reaction decreases markedly. (iii) Dialkyl ketones are not suitable as substrates because reactions proceed only in low yield with severe side reactions. These disadvantages can be overcome, since we found the rhodium(I) complex quite effective for the hydrosilylation of carbonyl compounds. We describe here a full account of our research on the asymmetric hydrosilylation of prochiral ketones, using a neutral rhodium(I) complex with chiral phosphine ligands as well as the mechanism of the induction of asymmetry.

Results and discussion

Asymmetric reduction of alkyl phenyl ketones and dialkyl ketones

The rhodium(I) complex with chiral phosphine ligands was prepared in situ by the reaction of $[Rh(1,5\text{-hexadiene})Cl]_2$ or $[Rh(1,5\text{-cyclooctadiene})Cl]_2$ with two equivalents of (—)-(*S*)- or (+)-(*R*)-benzylmethylphenylphosphine(BMPP) in degassed benzene.

Alkyl phenyl ketones, $RCOC_6H_5$, where R is methyl, ethyl, iso-propyl, tert-butyl and cyclohexyl were allowed to react with the monohydrosilane or dihydrosilane in the presence of the chiral rhodium catalyst (0.1—0.5 mol%) in benzene. The resulting optically active silyl ethers were solvolyzed using sodium methoxide in methanol to afford the corresponding 1-alkylbenzyl alcohols in nearly quantitative yields (eq. 1.)

$$RCOC_6H_5 + H\text{—}Si\equiv \xrightarrow{[Rh]^*} \underset{C_6H_5}{\overset{R}{\overset{*}{\diagdown\!\diagup}}}CH\text{—}OSi\equiv \xrightarrow{MeONa/MeOH} \underset{C_6H_5}{\overset{R}{\overset{*}{\diagdown\!\diagup}}}CH\text{—}OH \qquad (1)$$

$[Rh]^*$: $(BMPP)_2RhCl(S)$ (S = solvent)

The optically active silyl ethers of 1-alkylbenzyl alcohol, the hydrosilylation products, could be isolated by distillation and characterized by their spectra and elemental analyses. Absolute configuration and optical purity of the 1-alkylbenzyl alcohol thus obtained were determined on the basis of the known maximum rotation of the pure enantiomer.

The rate of the reaction was found to be slower when a monohydrosilane was employed and some heating was necessary to complete the reaction. Thus, the reactions were carried out at 40—50°C in the case of monohydrosilanes *. On the other hand, the rate of the reaction increased remarkably when a dihydrosilane was employed, i.e., an exothermic reaction occurred at ambient temperature in most cases. Accordingly, the reactions of dihydrosilane with alkyl phenyl ketone were allowed to start at 5—10°C.

Results are summarized in Table 1.

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* We employed dimethylphenylsilane and dimethylethylsilane as monohydrosilane for the reaction. Dimethylphenylsilane was found to be effective for all alkyl phenyl ketones. However, triethylsilane and dimethylethylsilane showed only poor reactivity toward alkyl phenyl ketones (except tert-butyl phenyl ketone) when the chiral rhodium(I) catalyst, $(BMPP)_2RhCl(S)$, was employed, although the same silane was found to react readily with acetophenone when a similar rhodium(I) complex, $(Ph_3P)_3RhCl$, was used without solvent [13].

TABLE 1

ASYMMETRIC REDUCTION OF ALKYL PHENYL KETONES VIA HYDROSILYLATION CATALYZED BY [BMPP]$_2$Rh(S)Cl (S = SOLVENT)

Entry No.	Ketone	Hydrosilane	Silyl ether [a] $[\alpha]_D^{20-23}$	Alcohol [a] $[\alpha]_D^{20-23}$	Configuration	Chemical yield (%) [b]	Optical yield (%) [c]
Ligand = (−)-(S)-BMPP							
1	$PhCOCH_3$	$PhMe_2SiH$	+20.8 [d]	+14.32 [e]	*R*	92	44
2	$PhCOC_2H_5$	$PhMe_2SiH$	+22.6	+8.74	*R*	96	50
3	$PhCOC_3H_7$-i	$PhMe_2SiH$	+24.5	+16.68 [f]	*R*	95	56
4	$PhCOC_2H_5$	Et_2SiH_2	−5.10	−2.90	*S*	98	17
5	$PhCOC_3H_7$-i	Et_2SiH_2	−6.33	−6.73 [f]	*S*	98	23
Ligand = (+)-(R)-BMPP							
6	$PhCOCH_3$	Et_2SiH_2	+5.10	+6.44 [e]	*R*	97	16
7	$PhCOC_2H_5$	Ph_2SiH_2	+18.50	+9.04	*R*	98	42
8	$PhCOC_3H_7$-i	Ph_2SiH_2	−9.08	−5.92 [f]	*S*	96	16
9	$PhCOC_3H_7$-i	$PhMeSiH_2$	−4.28	−4.32 [f]	*S*	93	12
10	$PhCOC_4H_9$-t	$EtMe_2SiH$	+14.23	+15.63 [f]	*R*	97	56
11	$PhCOC_4H_9$-t	$PhMe_2SiH$	−20.68	−14.91 [f]	*S*	92	54
12	$PhCOC_6H_{11}$-c	$PhMe_2SiH$	−21.80	−10.88 [d]	*S*	90	58
13	$PhCOC_6H_{11}$-c	Et_2SiH_2	+5.20	+3.55 [d]	*R*	95	19

[a] All optical rotations are for the neat liquid unless otherwise noted. [b] Yield of an alcohol (GLC analysis). [c] Optical yield is calculated from the specific rotation of the pure enantiomer which is reported in the literature [(*S*)-PhMeCHOH, $[\alpha]_D^{23}$ −52.5° (CH_2Cl_2, *c* 2.27) [22]; (*S*)-PhEtCHOH, $[\alpha]_D^{22}$ −28.1° (neat) [23]; (*S*)-Ph^{i}PrCHOH, $[\alpha]_D^{20}$ −47.7° (ether, *c* 7) [24]; (*R*)-Ph-t-BuCHOH, $[\alpha]_D^{20}$ +36.2° (ether, *c* 9) [25,26]; (*S*)-Ph(c-C_6H_{11})CHOH, $[\alpha]_D^{22}$ −28.27° (benzene, *c* 3.29) [26,27]] and calibrated for the optical purity of the chiral phosphine employed [(−)-(*S*)-BMPP, 62% e.e., (+)-(*R*)-BMPP, 77% e.e. for No. 6—11 and 66% e.e. for No. 12—13]. [d] Specific rotation in benzene (Entry No. 1, *c* 10.0; No. 12, *c* 3.41; No. 13, *c* 3.92). [e] Specific rotation in dichloromethane (Entry No. 1, *c* 1.50; No. 6, *c* 2.39). [f] Specific rotation in ether (Entry No. 3, *c* 7.26; No. 5, *c* 7.78; No. 8, *c* 7.41; No. 9, *c* 7.18; No. 10, *c* 9.26; No. 11, *c* 6.87).

In a similar manner, prochiral dialkyl ketones were hydrosilylated using the same chiral rhodium catalyst and converted to the corresponding optically active sec-alcohols in excellent yields. Results are summarized in Table 2.

It should be noted that dialkyl ketones were readily reduced to optically active sec-alcohols without any side reactions in excellent chemical yields and in fairly good optical yields, comparable to those attained in the case of alkyl phenyl ketones, by the use of dihydrosilanes. Our procedure therefore is the method of choice because; (i) the hydrosilylation of dialkyl ketones catalyzed by platinum(II) complexes was hampered by the severe side reaction [18], i.e., the formation of silyl enol ether, and (ii) the independently reported asymmetric reduction of ketones by catalytic hydrosilylation was limited to alkyl phenyl ketones except the case of benzyl methyl ketone, which was reduced to 2-phenylpropanol in only 1—5.3% optical yield by Kagan and coworkers using [(+)-DIOP]Rh(S)Cl as a chiral catalyst [18d].

As is seen from Tables 1 and 2, both the configuration and the optical yield of the resulting alcohols depend upon the structure of hydrosilanes employed. For example, iso-propyl phenyl ketone was reduced to (+)-(*R*)-2-methyl-1-phenylpropan-1-ol in 56% optical yield with the use of (−)-(*S*)-benzylmethylphenylphosphine [(*S*)-BMPP] as a chiral ligand and dimethylphenylsilane as a reducing agent, while (−)-(*S*)-2-methyl-1-phenyl-propan-1-ol was obtained in

TABLE 2

ASYMMETRIC REDUCTION OF PROCHIRAL DIALKYL KETONES VIA HYDROSILYLATION CATALYZED BY $[BMPP]_2Rh(S)Cl$ (S = SOLVENT)

Entry No.	Ketone	Hydrosilane	Silyl ether [a] $[\alpha]_D^{20-23}$	Alcohol [a] $[\alpha]_D^{18-26}$	Configuration	Chemical yield (%) [b]	Optical yield (%) [c]
Ligand = (—)-(S)-BMPP							
14	$n\text{-}C_4H_9COCH_3$	Et_2SiH_2	+3.20 [d]	+2.24	*S*	93	31
15	$t\text{-}C_4H_9COCH_3$	Et_2SiH_2	+3.96	+1.88	*S*	95	39
Ligand = (+)-(R)-BMPP							
16	$t\text{-}C_4H_9COCH_3$	Ph_2SiH_2	—4.01	—1.51	*R*	98	25
17	$i\text{-}C_4H_9COCH_3$	Et_2SiH_2	—2.66	—1.90	*R*	99	12
18	$n\text{-}C_6H_{13}COCH_3$	Et_2SiH_2	—1.38	—0.76	*R*	98	9
19	$c\text{-}C_6H_{11}COC_3H_7\text{-}n$	Et_2SiH_2	+0.80	+1.24	*R*	98	11
20	$c\text{-}C_6H_{11}COC_3H_7\text{-}i$	Et_2SiH_2	+0.10	+0.25	*S*	94	4
21	$c\text{-}C_6H_{11}COCH_3$	Ph_2SiH_2	+0.16	—1.73	*R*	92	40
22	$c\text{-}C_6H_{11}COC_3H_7\text{-}n$	Ph_2SiH_2	+0.96	+1.10	*R*	95	10
23	$c\text{-}C_6H_{11}COC_4H_9\text{-}t$	Ph_2SiH_2	—0.96	+7.23	*R*	90	43

[a] All optical rotations are for the neat liquid unless otherwise noted. [b] Yield of an alcohol (GLC analysis). [c] Optical yield is calculated from the specific rotation of the pure enantiomer which is reported in the literature [(*S*)-n-BuMeCHOH, $[\alpha]_D^{18}$ +11.68° (neat) [28]; (*S*)-t-BuMeCHOH, $[\alpha]_D^{20}$ +7.84° (neat) [29]; (*S*)-i-BuMeCHOH, $[\alpha]_D^{25}$ +24.6° (neat) [30]; (*S*)-n-C_6H_{13}MeCHOH, $[\alpha]_D^{25}$ +12.7° (neat) [30]; (*S*)-c-C_6H_{11}-MeCHOH, $[\alpha]_D^{23}$ +6.5° (neat) [30]; (*S*)-c-C_6H_{11}-i-PrCHOH, $[\alpha]_D^{25}$ +9.90° (neat) [31]; (*S*)-c-C_6H_{11}-t-BuCHOH, $[\alpha]_D^{26}$ —25.5° (neat) [31]] and calibrated for the optical purity of the chiral phosphine employed [(—)-(*S*)-BMPP, 62% e.e., (+)—(*R*)-BMPP, 77% e.e. for Entry No. 16, 66% e.e. for No. 17—23]. [d] Specific rotation in benzene, *c* 3.99.

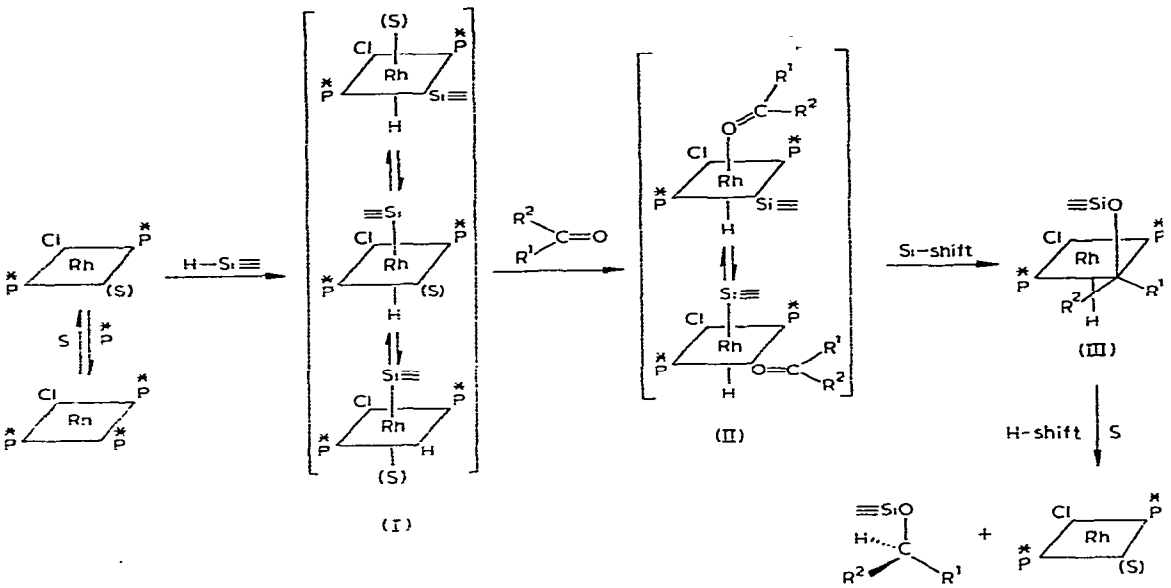
23% optical yield using the same chiral phosphine ligand and diethylsilane. These results clearly demonstrate that the stereochemical requirement for good matching of the chiral ligand, hydrosilane and ketone in the coordination sphere is a quite important factor in order to obtain the better optical yield.

Possible mechanism for the induction of asymmetry

As for the induction of asymmetry, we propose here a mechanism for the BMPP-rhodium(I) complex system based on the stereochemical consideration of the relationship between the configuration of the chiral phosphine and that of the resulting alcohol. As reported previously [15] the intermediacy of the α-silyloxyalkylrhodium complex is strongly suggested in the hydrosilylation of terpene ketones catalyzed by $(Ph_3P)_3RhCl$. Therefore, it is probable that the intermediate α-silyloxyalkylrhodium complex also plays a key role in the asymmetric induction in the present system. Accordingly, the proposed mechanism involves the following steps as shown in Scheme 2. (a) Oxidative addition of the hydrosilane to the rhodium(I) complex; (b) insertion of the ketone carbonyl into the resulting silicon—rhodium bond to form the diastereomeric α-silyloxyalkylrhodium intermediate III; (c) formation of an optically active silyl ether of the sec-alcohol by reductive elimination. Of these, step b must play the most important role in inducing asymmetry at the carbonyl carbon because this step determines a predominant configuration and the extent of enantiomeric excess of the product.

It is also conceivable that the hydrosilylation of ketones proceeds via alkoxyrhodium intermediates which arise from the insertion of ketone carbonyl into

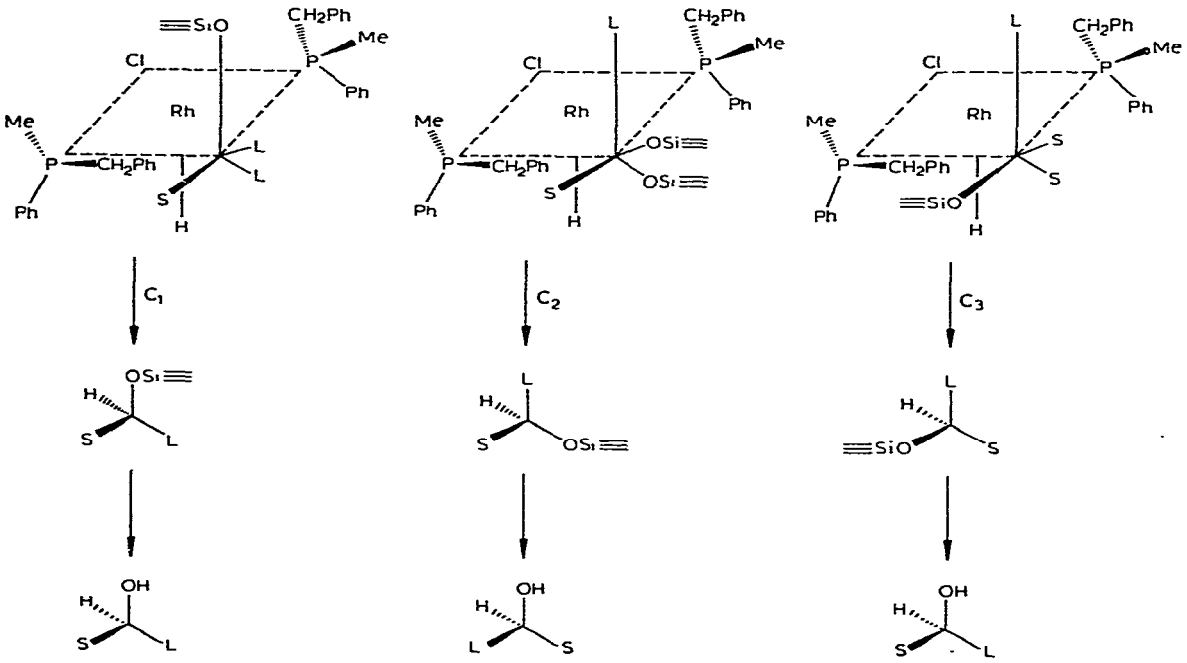
SCHEME 2



the hydridorhodium moiety in a manner similar to that of olefins. In fact, the intervention of an alkoxyrhodium complex has been proposed by Schrock and Osborn for the hydrogenation of ketones catalyzed by cationic rhodium complexes [3]. However, such a mechanism involving alkoxyrhodium intermediates cannot accomodate the observed changes in optical yields on changing the silane structure. Moreover, the fact that the asymmetric hydrogenation of acetophenone catalyzed by a cationic rhodium complex with the same chiral phosphine, $[\{(+)\text{-BMPP}\}_2Rh(S)_2H_2]^+ClO_4^-$, has been found to give (*R*)-1-phenylethanol [6], which has the opposite configuration to that obtained by means of asymmetric hydrosilylation, reinforces the argument that there is a difference in the key steps between hydrogenation and hydrosilylation of ketones.

It is reasonable to assume the square-pyramidal structure of the α-silyloxyalkylrhodium complex III on account of the established structures of the silylhydrido complex [32,13c] and dihydrido complexes [33] derived from tris(triphenylphosphine)chlororhodium, where the two phosphines form a trans configuration with each other. The configuration of the complex III in Scheme 2 depends upon the relative bulkiness of the substituents of ketones, those of the chiral phosphine and the silyloxy groups. For example, when the silyloxy group is bulkier than either of the substituents of the ketone, i.e., ≡SiO > L > S, stereochemical considerations, using a Dreiding model of the complex III, lead us, to the conclusion that the silyloxy group should occupy the quasi-apical position which is the least hindered site and lies between methyl and benzyl group of the chiral phosphines. It follows then that the substituent L lies between the methyl and phenyl groups and the substituent S lies between the benzyl and phenyl groups. The conformation which satisfies these requirements is depicted as C_1 in Scheme 3 in which (*S*)-BMPP is employed as a ligand. In a similar manner, when the order of bulkiness is L > ≡SiO > S, the most stable conformation

SCHEME 3



is C_2, and when that is L > S > ≡SiO, the most stable conformation is C_3. As is immediately seen from Scheme 3, the alcohol derived from C_1 has the same configuration as that derived from C_3, whereas the alcohol derived from C_2 has an opposite configuration when the priority sequence, as proposed by Cahn, Ingold and Prelog [20], of the substituents on the carbon is identical in each case.

According to the proposed mechanism, the relationship between the configuration of the chiral phosphine and that of the resulting alcohol should fall into six different cases as shown in Table 3 on account of both the bulkiness and the priority sequence.

TABLE 3

RELATIONSHIP BETWEEN THE BULKINESS SEQUENCE AND CONFORMATIONAL REQUIREMENT AT CARBONYL CARBON

Case	Bulkines	Configurational relationship [a]	Conformation of the complex III
	Priority Sequence L > S		
A	≡SiO > L > S	opposite	C_1
B	L > ≡SiO > S	same	C_2
C	L > S > ≡SiO	opposite	C_3
	Priority Sequence L < S		
A'	≡SiO > L > S	same	C_1
B'	L > ≡SiO > S	opposite	C_2
C'	L > S > ≡SiO	same	C_3

[a] Relationship between the configuration of the chiral phosphine and that of the resulting alcohols.

The preferred configuration, i.e., *R* and *S*, of the resulting alcohols is consistently predicted on the basis of the mechanism just mentioned above, when the bulkiness of the silyloxy groups is estimated empirically as follows for alkyl phenyl ketones: C-Hex > t-Bu > $PhMe_2SiO$ > Ph > $EtMe_2SiO$ > Et_2SiHO ⩾ i-Pr > Ph_2SiHO > PhMeSiHO > Et > Me. Although it seems rather unusual that the Et_2SiHO group is estimated to be bulkier than the Ph_2SiHO group, some electronic effect of phenyl(s) on silicon would reduce the apparent bulkiness of the silyloxy moiety in the coordination sphere. The correlations between experimental results and the predictions are shown in Table 4 (Entry No. 1—13), which demonstrate that the predicted preferred configuration of the resulting alcohols exactly matches the observed one without exception, (see also Table 1.)

A similar prediction is possible for dialkyl ketones. In the asymmetric reduction of dialkyl ketones, however, only dihydrosilanes were employed as reducing agent since the reaction using monohydrosilanes resulted in poor induction of asymmetry. Moreover, the stereochemical interaction operating in the coordination sphere of the intermediate complex, III, formed from dialkyl ketones would be slightly different from that estimated in the case of alkyl phenyl ketones. It should be taken into account that phenyl has an electronic effect as well as its steric effect on the extent of congestion in the whole coordination sphere, which is caused by the substituents of ketone, those of phosphorus and the silyloxy group. These effects cannot be expected for simple alkyl substituents.

TABLE 4

PREDICTED CONFIGURATIONAL RELATIONSHIPS

Entry [a] No.	Substituents			Classification [b]	Configurational relationship [a]
	L	S	≡SiO		
1	Ph	Me	$PhMe_2SiO$	A	opposite
2	Ph	Et	$PhMe_2SiO$	A	opposite
3	Ph	i-Pr	$PhMe_2SiO$	A	opposite
4	Ph	Et	Et_2SiHO	B	same
5	Ph	i-Pr	Et_2SiHO	B	same
6	Ph	Me	Et_2SiHO	B	same
7	Ph	Et	Ph_2SiHO	B	same
8	Ph	i-Pr	Ph_2SiHO	C	opposite
9	Ph	i-Pr	PhMeSiHO	C	opposite
10	t-Bu	Ph	$EtMe_2SiO$	C′	same
11	t-Bu	Ph	$PhMe_2SiO$	B′	opposite
12	c-Hex	Ph	$PhMe_2SiO$	B′	opposite
13	c-Hex	Ph	Et_2SiHO	C′	same
14	n-Bu	Me	Et_2SiHO	B	same
15	t-Bu	Me	Et_2SiHO	B	same
16	t-Bu	Me	Ph_2SiHO	B	same
17	i-Bu	Me	Et_2SiHO	B	same
18	n-Hex	Me	Et_2SiHO	B	same
19	c-Hex	n-Pr	Et_2SiHO	B	same
20	c-Hex	i-Pr	Et_2SiHO	C	opposite
21	c-Hex	Me	Ph_2SiHO	B	same
22	c-Hex	n-Pr	Ph_2SiHO	B	same
23	c-Hex	t-Bu	Ph_2SiHO	C′	same

[a] See Table 1 and 2. [b] See Table 3.

On account of these points, the bulkiness of the silyloxy groups is estimated as follows: C-Hex > t-Bu > i-Bu > i-Pr > n-Bu > Et_2SiHO > Ph_2SiHO > n-Pr > Me for dialkyl ketones, which is largely in agreement with that evaluated for alkyl phenyl ketones. In these cases, the preferred configuration (R and S) of the produced alcohols are also consistently predicted in accordance with the given mechanism. Results are summarized in Table 4 (Entry No. 14—23) (see also Table 2).

It should be noted that the mechanism of asymmetric induction in the homogeneous catalytic system is clearly explained only on the basis of a stereochemical point of view like usual organic asymmetric reactions.

At this point, a question arises: Does the actual catalyst operating in the present system happen to be same as that generated from the cationic rhodium complex precursor [18b], $[Rh\{(R)\text{-BMPP}\}_2H_2(S)_2]^+ClO_4^-$? It is possible for the present non-cationic complex, $[(R)\text{-BMPP}]_2Rh(S)Cl$ to lose chloride as a counter anion by the action of hydrosilane, giving a cationic species. In order to clarify this point, the results obtained by using the present non-cationic rhodium complex are compared with those obtained with the cationic rhodium complex. Namely, the preferred configurations of the resulting alcohols are predicted by applying the rule described above to the cationic rhodium complex system. Results are summarized in Table 5, which includes the further outcome obtained by Hayashi, Yamamoto and Kumada after their first report had been published [21].

In Table 5 are also listed the optical yields attained by using the non-cationic rhodium complex when the same substrates were employed. On the prediction of configuration the bulkiness order is estimated as follows in agreement with the case of the non-cationic rhodium complex system as described above: t-Bu > Ph_2MeSiO > $PhMe_2SiO$ > Et_2MeSiO > Ph ≥ Me_3SiO > Et_2SiHO > i-Pr > Ph_2SiHO ~ PhMeSiHO > Et > Me. As is immediately seen from the Table 5, the predicted configurations largely match the observed ones except for three experiments (Entry No. 2, 5 and 12) in which trimethylsilane is employed. In the exceptional cases, however, the optical yields are low, i.e., around 5% e.e. This fact indicates that the difference in the transition state energy, $\Delta\Delta G^{\ddagger}$, between two diastereomeric transition states is very small, and suggests that the bulkiness of Me_3SiO group is comparable to that of phenyl in the coordination spere of the cationic rhodium complex. Accordingly, if one estimates that the Me_3SiO group is slightly larger than phenyl, the observed configurations correspond well to the predicted ones, and Entry No. 14 becomes the only exception. However, it would be better to treat the former three experiments as exceptions since the optical yield realized in the case of tert-butyl phenyl ketone is relatively high, i.e., $\Delta\Delta G^{\ddagger}$ is large. Anyhow, the inconsistency observed between Entry No. 2, 5, 12 and Entry No. 14 when trimethylsilane is employed may indicate a limit of the application of the prediction, which has not been seen in the case of the noncationic rhodium complex catalyzed reactions. On the other hand, the optical yields attained by both catalytic systems are comparable for the reactions of monohydrosilanes, but not for those of dihydrosilanes (see Entry No. 8 and 9).

Consequently, it can be said on the basis of the comparisons that the actual catalyst of the cationic rhodium complex is closely related to that of non-

TABLE 5

COMPARISON OF THE RESULTS OF CATIONIC RHODIUM COMPLEX CATALYZED ASYMMETRIC HYDROSILYLATION OF KETONES WITH THOSE OF NON-CATIONIC RHODIUM COMPLEX CATALYZED REACTIONS

Entry No.	Ketone	Hydrosilane	Cationic system				Non-cationic system [c]
			Optical yield (%)	Configuration (observed)	Corresponding case [a]	Configuration (predicted) [b]	Optical yield (%)
1	PhCOMe	$PhMe_2SiH$	31.6	*S*	A	*S*	44
2	PhCOMe	Me_3SiH	5.1	*S*	B	*R*	
3	PhCOMe	Ph_2SiH_2	14.6	*R*	B	*R*	
4	PhCOEt	$PhMe_2SiH$	43.1	*S*	A	*S*	50
5	PhCOEt	Me_3SiH	6.4	*S*	B	*R*	
6	PhCOEt	$PhMe_2SiH$	20.3	*S*	A	*S*	
7	PhCOEt	Et_2MeSiH	1.3	*S*	A	*S*	
8	PhCOEt	Et_2SiH_2	2.0	*R*	B	*R*	17
9	PhCOEt	Ph_2SiH_2	4.4	*R*	B	*R*	42
10	PhCOEt	$PhMeSiH_2$	11.7	*R*	B	*R*	
11	PhCOPr-i	$PhMe_2SiH$	56.3	*S*	A	*S*	56
12	PhCOPr-i	Me_3SiH	3.7	*S*	B	*R*	
13	t-BuCOPh	$PhMe_2SiH$	61.8	*S*	B′	*S*	54
14	t-BuCOPh	Me_3SiH	28.1	*R*	C′	*R*	
15	t-BuCOPh	Et_2SiH_2	3.3	*R*	C′	*R*	
16	t-BuCOMe	Et_2SiH_2	23.0	*R*	B	*R*	39
17	t-BuCOMe	Ph_2SiH_2	22.5	*R*	B	*R*	25

[a] See Table 3. [b] See Scheme 3 and Table 4. [c] See Tables 1 and 2.

cationic rhodium complex, but is not the same, i.e., the effect of the counter anion, ClO_4^-, should be taken into account for the cationic rhodium complex catalyzed reactions.

Experimental

Measurements

Boiling points were uncorrected. Infrared spectra were recorded on a Hitachi EPI-G3 spectrophotometer, using samples as neat liquid. Nuclear magnetic resonance spectra were obtained by the use of a Varian HA-100 or a Varian T-60 spectrometer, using TMS as the internal standard. Analytical gas chromatography (GLC) was carried out on a Shimadzu GC-3BT, GC-3BF or GC-5A using a column packed with 20% SE-30, 10% QF-1 and 3% OV-17. Optical rotations were measured with a Yanagimoto OR-50 automatic polarimeter.

Materials

Hydrosilanes were prepared by known methods. Carbonyl compounds are commercially available and were purified by distillation. (—)-(*S*)-Benzylmethylphenylphosphine [(—)-(*S*)-BMPP] was prepared by Mislow's method [34b] using *N,N*-diethylaniline as a base for the reduction of (+)-(*R*)-benzylmethylphenylphosphine oxide by trichlorosilane. Similarly, (+)-(*R*)-benzylmethylphenylphosphine [(+)-(*R*)-BMPP] was prepared using triethylamine as a base. The optical purity of the chiral phosphine was determined by quaternization using n-propyl bromide: [(—)-PhMe($PhCH_2$)P^+Pr^n]Br^-, $[\alpha]_D^{25}$ —22.82° (methanol, *c* 1.55, 62% e.e.); [(+)-PhMe($PhCH_2$)P^+Pr^n]Br^-, $[\alpha]_D^{25}$ +28.34° (methanol, *c* 1.63, 77% e.e.) and $[\alpha]_D^{25}$ +24.44° (methanol, *c* 1.13, 66% e.e.). The value for the pure enantiomer was reported by Horner et al. [34a]: $[\alpha]_D^{25}$ +36.8° (methanol, *c*, 1.507).

Preparation of catalyst solution

The optically active catalyst was prepared in situ by the reaction of [Rh(1,5-hexadiene)Cl]$_2$ or [Rh(1,5-cyclooctadiene)Cl]$_2$ with (—)-(*S*)-BMPP or (+)-(*R*)-BMPP in benzene at room temperature. In a typical experiment, 25 mg (5.07×10^{-5} mol) of [Rh(COD)Cl]$_2$ was dissolved in 5 ml of degassed benzene with stirring under argon. Then, 60 μl (2.80×10^{-4} mol) of (+)-(*R*)-BMPP was added to the solution using a microsyringe and the solution was stirred for 15 min.

Asymmetric reduction of ketones via hydrosilylation

A mixture of the ketone (30 mmol) and hydrosilane (33 mmol) in 10 ml of degassed benzene was added to the catalyst solution (5 ml) described above and stirred at the appropriate temperature (40—50°C for monohydrosilane and 5—25°C for dihydrosilane) for 3—48 h. The completion of the reaction was checked by GLC using a column packed with 3% SE-30. Then, 0.5% methanol solution * of sodium methoxide was added to the reaction mixture and stirred for an hour. After the solvent was evaporated, the residue was submitted to

(continued on p. 96)

* The solvolysis of bulky silyl ethers required more severe conditions, e.g., for the alcoholysis of c-C_6H_{11}PhCHOSiMe$_2$Ph and t-BuPhCHOSiMe$_2$Ph, n-propyl alcohol was employed as solvent, and heating under reflux for several hours was necessary to complete the reaction.

TABLE 6

IDENTIFICATION OF OPTICALLY ACTIVE SILYL ETHERS $R^1R^2{}^*CH{-}OSiR^3R^4R^5$

Entry No	R^1	R^2	R^3	R^4	R^5	B.p. (°C/Torr.)	Analysis found (calcd.) (%)		IR(cm^{-1}) $\nu_{C=O}$	NMR(δ)(CCl_4)	
							C	H		methine	SiH
1	Me	Ph	Me	Me	Ph	92/0.18	74.85 (74.95)	7.58 (7.86)		4.81(quartet, J 7 Hz)	
2	Et	Ph	Me	Me	Ph	110/0.25	75.53 (75.50)	7.96 (8.20)		4.58(t, J 6 Hz)	
3	i-Pr	Ph	Me	Me	Ph	113/0.25	76.18 (76.00)	8.47 (8.50)		4.34(d, J 7 Hz)	
4	Et	Ph	Et	Et	H	71/0.19	70.28 (70.21)	10.07 (9.97)	2110	4.58(t, J 6 Hz)	4.42(quintet, J 2 Hz)
5	i-Pr	Ph	Et	Et	H	76/0.25	70.97 (71.12)	10.44 (10.23)	2110	4.35(d, J 7 Hz)	4.40(quintet, J 2 Hz)
6	Me	Ph	Et	Et	H	114/19	68.93 (69.17)	9.83 (9.68)	2110	4.90(quartet, J 7 Hz)	4.49(quintet, J 2 Hz)
7	Et	Ph	Ph	Ph	H	150/0.35	78.95 (79.20)	6.88 (6.96)	2115	4.70(t, J 7 Hz)	5.39(s)
8	i-Pr	Ph	Ph	Ph	H	152/0.32	79.69 (79.47)	7.00 (7.28)	2120	4.48(d, J 7 Hz)	5.40(s)
9	i-Pr	Ph	Me	Ph	H	116/1.2	75.23 (75.50)	8.34 (8.20)	2120	4.30(d, J 7 Hz) (minor) 4.39(d, J 7 Hz) (major)	4.96(quartet, J 2 Hz) (major) 5.19(quartet, J 2 Hz) (minor)
10	t-Bu	Ph	Me	Me	Et	132/26	72.02 (71.93)	10.22 (10.46)		4.58(s)	
11	t-Bu	Ph	Me	Me	Ph	110/0.28	76.32 (76.45)	8.52 (8.78)		4.26(s)	
12	c-Hex	Ph	Me	Me	Ph	143/0.2	77.80 (77.72)	8.85 (8.70)		4.20(s)	

13	c-Hex	Ph	Et	Et	H	111/0.1	73.56 (73.86)	10.21 (10.21)	2090	4.25(d, *J* 6 Hz)	4.30(quintet, *J* 2 Hz)
14	Me	n-Bu	Et	Et	H	65/10	63.85 (63.76)	12.72 (12.84)	2100	3.70(m)	4.38(quintet, *J* 2 Hz)
15	Me	t-Bu	Et	Et	H	70/20	63.55 (63.76)	12.66 (12.84)	2100	3.55(quartet, *J* 7 Hz)	4.54(quintet, *J* 2 Hz)
16	Me	t-Bu	Ph	Ph	H	105/0.45	75.73 (76.00)	8.20 (8.50)	2120	3.82(quartet, *J* 7 Hz)	5.76(s)
17	Me	i-Bu	Et	Et	H	75/20	63.48 (63.76)	12.83 (12.84)	2100	3.77(sextet, *J* 6 Hz)	4.32(quintet, *J* 2 Hz)
18	Me	n-Hex	Et	Et	H	107/17	66.77 (66.59)	12.92 (12.98)	2100	3.69(m)	4.34(quintet, *J* 2 Hz)
19	c-Hex	n-Pr	Et	Et	H	90/1.2	69.60 (69.35)	12.32 (12.50)	2100	3.38(m)	4.41(quintet, *J* 2 Hz)
20	c-Hex	i-Pr	Et	Et	H	86/1.1	69.46 (69.35)	12.51 (12.50)	2100	3.12(m)	4.47(quintet, *J* 2 Hz)
21	c-Hex	Me	Ph	Ph	H	151/0.1	77.27 (77.36)	8.35 (8.44)	2110	3.66(m)	5.37(s)
22	c-Hex	n-Pr	Ph	Ph	H	149/0.1	77.86 (78.05)	8.83 (8.93)	2120	3.60(m)	5.40(s)
23	c-Hex	t-Bu	Ph	Ph	H	173/0.3	78.28 (78.28)	9.11 (9.15)	2115	3.15(m)	5.46(s)

column chromatography on silica gel. The optically active alcohol was obtained from the benzene/ether eluate in 80—95% yield. For the measurement of the optical rotation of the alcohol, a further distilled sample was employed. The intermediately formed optically active silyl ether, the hydrosilylated product, was distilled under reduced pressure to give a pure sample. Results are summarized in Tables 1 and 2. Physical constants, analytical data for the identification of the silyl ethers are listed in Table 6. Two examples of the typical procedure are given below.

Asymmetric reduction of tert-butyl phenyl ketone via hydrosilylation using dimethylethylsilane catalyzed by [(+)-BMPP]$_2$ Rh(S)Cl

To a 5 ml degassed benzene solution of the chiral catalyst (0.114 mmol) was added a mixture of tert-butyl phenyl ketone (4.50 g, 30 mmol) and dimethylethylsilane (2.90 g, 33 mmol) in 10 ml of degassed benzene. The mixture was heated at 40°C over a period of 12 h. GLC analysis showed more than 98% yield production, based on the ketone, of 2,2-dimethyl-1-phenylpropyl dimethy ethylsilyl ether. The reaction mixture was diluted exactly to 50 ml with benzene and the solution was divided into two 25 ml fractions using volumetric flasks. One of the fractions was evaporated and distilled under reduced pressure to afford the silyl ether (2.93 g, 82%), bp. 132°C/26 Torr., $[\alpha]_D^{23}$ +14.23° (neat). The other fraction, after evaporation of solvent, was solvolyzed using 25 ml of 0.5% methanol solution of sodium methoxide at ambient temperature. The methanolysis was complete within an hour. GLC analysis displayed the production of 2,2-dimethyl-1-phenylpropanol in 97% yield based on the ketone. After the methanol was evaporated, the residue was submitted to column chromatography on silica gel. The alcohol was obtained from the benzene/ether eluate and further distilled under reduced pressure for the measurement of optical rotation (2.01 g, 88%), bp. 110°C/15 Torr. (lit. [35] 95—100°C/10 Torr.), $[\alpha]_D^{21}$ +15.63° (ether, *c* 9.26).

Asymmetric reduction of 3,3-dimethylbutan-2-one via hydrosilylation using diethylsilane catalyzed by [(+)-BMPP]$_2$Rh(S)Cl

A mixture of 3,3-dimethylbutan-2-one (5.00 g, 50 mmol), diethylsilane (4.58 g, 52 mmol) and the catalyst (5.07×10^{-2} mmol) in 15 ml degassed benzene was stirred in a reaction flask cooled with cold water (5—10°C) for 2 h. Then, the reaction mixture was gradually warmed to 20—25°C and stirred for an additional 2 h. GLC analysis showed a quantitative production of 3,3-dimethyl-2-butyl diethylsilyl ether. In a similar manner to that described above, one half of the reaction mixture was distilled under reduced pressure to afford the silyl ether (4.23 g, 90% based on the ketone), bp. 70°C/20 Torr., $[\alpha]_D^{21.5}$ +3.96° (neat). The other half was solvolyzed by adding 25 ml of 0.5% methanol solution of sodium methoxide at 15—20°C for an hour. GLC analysis showed the production of 3,3-dimethylbutan-2-ol in 95% yield based on the ketone. After evaporation of the methanol, the residue was dissolved in 30 ml of ether and stirred with 25 ml of 2N KOH for 6 h at ambient temperature. The ether layer was separated and the water layer was extracted with ether. After the combined ether extract was dried over anhydrous magnesium sulfate and concentrated, the residue was distilled to provide the pure alcohol. (1.91 g, 75%) bp. 120°C/760 Torr., (lit [36] 120—120.6°C/760 Torr.), $[\alpha]_D^{21.5}$ +1.88° (neat).

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